Treatment of Hydraulic Fracturing Fluids in Petroleum Wastewater Using Physical and Biological Techniques

A THESIS

SUBMITTED TO THE GRADUATE SCHOOL

IN PARTIAL FULFILLMENT OF THE REQUIREMENT

FOR THE DEGREE

MASTER OF SCIENCE

BY

OLUDAMILOLA ALALADE

ADVISOR: DR. JOHN PICHTEL

BALL STATE UNIVERSITY

MUNCIE, INDIANA

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Committee Chairperson	Date
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

CHAPTER 1: INTRODUCTION

Hydraulic fracturing ('fracking') is defined as the process of creating and propagating a fracture within a rock layer by means of applying hydraulic pressure in order to release petroleum, natural gas, coal seam gas, or other potential fuels for extraction. The energy from the injection of a highly pressurized fluid, such as water, creates new channels in the strata which can increase extraction rates and recovery of fossil fuels (Ryan, 2012).

The injected fluid is typically a slurry of water, so-called proppants, and chemical additives. The proppant is a mixture of durable solids, often containing grains of sand, ceramic, or other particulates that prevent fractures from closing when the fluid injection is halted. Chemical additives are used for many purposes, for example as biocides, control of iron oxide formation, and surfactants. About 750 chemicals are listed as additives for hydraulic fracturing according to a 2011 report to the US Congress (Waxman and Markey, 2011).

Although highly effective for recovery of petroleum and natural gas, hydraulic fracturing has become a significant issue due to concerns about public health and possible environmental contamination. A number of papers have described the effects of hydraulic fracturing on surface water quality, groundwater quality, and soil properties. Likewise, many studies have attempted to correlate specific human health impacts to hydraulic fracturing. The technology has already been banned in some countries, for example France, Bulgaria, Germany and Scotland. Several states within the United States have likewise banned hydraulic fracturing due to health and environmental concerns.

Hydraulic fracturing at a single field may require millions of gallons of relatively clean water and the process may impart significant impacts to local ecosystems (e.g., groundwater

depletion and pollution). Once the wastewater has been brought to the surface, it is either disposed or reused. Fracking wastewater is enriched in total dissolved solids, total suspended solids, metals, dispersed oil, dissolved and volatile organic compounds, Hydraulic Fracturing Fluid additives, and other contaminants to varying degrees; therefore, the operators face significant management challenges face operators (Stewart, 2013). Fracking wastewater must be managed in ways that both reduce the operational costs as well as are protective of the environment. Management practices vary widely across the United States and in some instances across a single oil and gas field (US DOE, 2006). Selection of a management option for Fracking wastewater at a site varies based on the following (NPC, 2011):

1. Chemical and physical properties of the wastewater.
2. Volumes, duration, and flow rate generated.
3. Desired end-use of the wastewater.
4. Treatment and disposal options allowed by state and federal regulations.
5. Technical and economic feasibility of a particular option, including transportation.
6. Availability of suitable infrastructure for management.
7. Willingness of companies to employ a particular technology or management option, including concerns about potential liability.

Wastewater recycling is not a mainstream practice among oil and gas companies, because the procedure is expensive, and, until recently, most oil and gas companies disposed of all wastewater. Presently, some companies are treating the wastewater for reuse for drilling or other purposes. There is a need in the oil and gas exploration industries to evaluate various methods of reusing and recycling drilling wastewater, particularly that which is contaminated with fracking

fluids. The reported research project focuses on water recycling and cleaning techniques using sorption and biodegradation processes.

LITERATURE REVIEW

Hydraulic Fracturing

Onshore domestic natural gas and oil production has experienced rapid growth over the past decade due to advances in horizontal drilling and hydraulic fracturing in shale formations. 'Unconventional wells' are defined as those drilled horizontally, allowing the borehole to bend 90 degrees and penetrate the target shale formation laterally up to thousands of meters (Kerr, 2010). Injecting a mixture of water, sand, and chemicals (collectively known as fracking fluid) at extremely high volumes (15,000 m^3 per well) and under high pressures into unconventional wells fractures the target geologic formation and releases a portion of the tightly trapped natural gas or oil for collection at the surface (Gregory et al., 2011).

Water and sand comprise the majority of the fluid composition (approx. 99.5%) while the remainder is an unspecified mixture of chemicals including acids, biocides, and surfactants (Gregory et al., 2011). Water that returns to the surface after injection is known as 'flowback' water, and once the hydrocarbon product is collected the returning water is termed 'produced' water. This wastewater is often stored on site before being transported to deep well injection sites or water treatment facilities for salt and chemical removal (Entrekin et al., 2011).

Relevant challenges confronting the gas and oil industries include reducing water usage, recycling water, finding suitable treatment technologies for wastewater, and minimizing the environmental impacts of wastewater disposal (Aaron, 2013).

Composition of Hydraulic Fracturing Fluids

Oil and gas production chemicals can be either a mixture, or a pure compound which contains active ingredients that serve desired purposes. Utilization of fracking fluids has become a significant concern as regards potential hazards to public health and the environment. Some, but not all, states have established requirements for unconventional gas and oil production (Rahm, 2011; 2013). Many oil and gas companies list all the chemicals they use in the production of fracking fluid on their websites, while others make the list only available on the Hydraulic Fracturing Chemical Registry (FracFocus, 2015).

Fracking fluids are classified into different categories based on their uses (Petro Wiki, 2015) and include: viscosified water-based fluids, non-viscosified water-based fluids, gelled oil-based fluids, acid-based fluids, and foam fluids. Water-based fluids are the most common and efficient because of the availability of large volumes of water. Approximately 98 to 99.5% water comprises the latter category of fluids (FracFocus, 2015). Additives consist of scale inhibitors, friction reducers, pH adjusters, proppants (propping agents), clay stabilizers, biocides, gelling and foaming components, surfactants, cross-linkers, breakers, corrosion inhibitors, and iron controlling agents. Table 1 provides the components of many documented fracking fluids (Stringfellow, 2014).

In hydraulic fracturing projects not all additives are necessarily used -- a suite of additives can be applied, if needed, to serve selected purposes. For example, surfactants can be used as both a gelling agent and a cross-linker (Stringfellow and Domen, 2014). During oil and gas production, different chemicals may be added during drilling and fracturing activities (Waxman and Markey, 2011; Deutch and Holditch 2001). Detailed information about fracking fluid composition was compiled by Stringfellow et al. (2014).

Table 1. Common chemical components of hydraulic fracturing fluids.

Chemical name	CAS no.	Formula
Acetaldehyde	75-07-0	C_2H_4O
Acetic acid	64-19-7	C_2H_4O2
Acetone	67-64-1	C_3H_6O
Adipic acid	124-04-9	$C_6H_{10}O_4$
Alkyl dimethyl benzyl ammonium chloride	68424-85-1	Various
Ammonium chloride	12125-02-9	C_lH_4N
Ammonium persulfate	7727-54-0	$(NH_4)_2S_2O_8$
Ammonium sulfate	7783-20-2	$(NH_4)_2SO_4$
Borate salts	Various	Various
Boric acid sodium salt	1333-73-9	Na_3BO_3
Calcium chloride	10043-52-4	CaC_{l2}
Calcium peroxide	1305-79-9	CaO_2
Carboxymethyl guar	39346-76-4	Various
Choline chloride	67-48-1	$C_5H_{14}C_lNO$
Citric acid	77-92-9	$C_6H_8O_7$
Copolymer of acrylamide and sodium acrylate	25987-30-8	Various
Copper compounds	Various	Various
Didecyl dimethyl ammonium chloride	7173-51-5	$C_{22}H_{48}C_lN$
Diesel fuel	Various	Various
Diethanolamine	111-42-2	$C_4H_{11}NO_2$
Ester salt	Various	Various
Ethanol	64-17-5	C_2H_6O
Ethyl methyl derivatives	Various	Various
Ethylene glycol	107-21-1	$C_2H_6O_2$
Formic acid	64-18-6	CH_2O_2
Fumaric acid	110-17-8	$C_4H_4O_4$
Glutaraldehyde	111-30-8	C_5H_8O
Glycol ethers	Various	Various
Guar gum	9000-30-0	Various
Isopropanol	67-63-0	C_3H_8O
Magnesium oxide	1309-48-4	MgO
Magnesium peroxide	14452-57-4	MgO_2
Methanol	67-56-1	CH_4O
Monoethanolamine	141-43-5	C_2H_7NO

Table 1 continued.

Chemical name	CAS no.	Formula
Monoethylamine	75-04-7	C_2H_7N
N,n-dimethyl formamide	68-12-2	C_3H_7NO
Naphthalene	91-20-3	$C_{10}H_8$
N,n-dimethyl formamide	68-12-2	C_3H_7NO
Naphthalene	91-20-3	$C_{10}H_8$
Petroleum distillate	64741-85-1	Various
Phosphonic acid salt	Various	Various
Polyacrylamide	9003-05-8	$(C_3H_5NO)n$
Polyglycol ether	Various	Various
Potassium carbonate	584-08-7	K_2CO_3
Potassium chloride	7447-40-7	KC_l
Potassium hydroxide	1310-58-3	KOH
Potassium metaborate	13709-94-9	BKO_2
Potassium persulfate	7727-21-1	$K_2O_8S_2$
Propargyl alcohol	107-19-7	C_3H_4O
Pyridinium	16969-45-2	C_5H_6N
Quaternary ammonium chloride	61789-71-1	Various
Sodium carbonate	497-19-8	Na_2CO_3
Sodium chloride	7647-14-5	NaCl
Sodium erythorbate	6381-77-7	$C_6H_7NaO_6$
Sodium hydroxide	1310-73-2	NaOH
Sodium lauryl sulfate	151-21-3	$C_{12}H_{25}NaO_4S$
Sodium persulfate	7775-27-1	$Na_2O_8S_2$
Sodium polycarboxylate	Various	Various
Sodium tetraborate decahydrate	1303-96-4	B_4O_7•2Na•$10H_2O$
Tetrakis hydroxymethyl-phosphonium sulfate	55566-30-8	$(C_4H_{12}O_4P)2O_4S$
Tetramethyl ammonium chloride	75-57-0	$C_4H_{12}ClN$
Thioglycolic acid	68-11-1	$C_2H_4O_2S$
Thiourea	62-56-6	CH_4N_2S
Tributyl tetradecyl phosphonium chloride	81741-28-8	$C_{26}H_{56}PCl$
Triethanolamine zirconate	101033-44-7	$C_{24}H_{56}N_4O_{12}Zr$
Zirconium hydroxy lactate sodium complex	113184-20-6	$C_{12}H_{19}NaO_{16}Zr$
Zirconium nitrate	13746-89-9	$Zr(NO_3)_4$
Zirconium sulfate	14644-61-2	$Zr(SO_4)_2$
1-Bromo-3-chloro-5,5-dimethylhydantoin	16079-88-2	$C_5H_6BrClN_2O_2$
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	$C_3H_2Br_2N_2O$
2-Bromo-3-nitrilopropionamide	1113-55-9	$C_3H_3BrN_2O$
2-Butoxyethanol	111-76-2	$C_6H_{14}O_2$

Adopted from: Henry and Edward, 2011; Stringfellow et al., 2014; Pichtel, 2016.

Treatment Technologies for Hydraulic Fracturing Fluids

A range of technologies, both chemical and physical, are available for the removal of oil and other contaminants from drilling-related wastewater. Technologies vary in terms of complexity of operation, portability, and cost. Both bench-scale and engineered systems for treatment of drilling water will be presented here.

Bench-Scale Systems for Treatment of Drilling Wastewater

Use of Natural Materials as Sorbents

'Sorption' may be defined as a physical and chemical process by which one substance becomes attached to another. Specific categories of sorption include: (1) absorption, i.e., the incorporation of a substance in one state into another of a different state (Badot and Pierre-Marie, 2010) (e.g., liquids being absorbed by a solid, or gases being absorbed by a liquid); and (2) adsorption – the physical adherence or bonding of ions and molecules onto the surface of another phase (e.g., a charged molecule in soil adsorbed to a clay surface).

In a study by Annuciado et al. (2005), various types of vegetable fibers including coir (*Cocos nucifera*), silk floss (*Chorisia speciose*) sponge gourd (*Luffa cylindrical*), and sisal (*Agave sisalana*), were used in a packed bed sorption process for treatment of oil wastewater. Also tested were mixed leaf residues and mixed sawdust. Crude oil was mixed with deionized water, and fibrous material was placed on the oily surface. After 24 hours the vegetable material was removed from the mixture using a nylon collector. Several of the plant residues were found to successfully remove a significant proportion of added oil.

Cotton grass fiber is recovered from peat bogs via a purifying and separating process (Suni et al., 2004). In most cases this product is disposed; however, due to its hydrophobic and oil-absorbing properties it may be beneficial as a sorbent for oil. A study was implemented

(Kosunen, 2004) where sorbent mats were constructed by combining cotton grass fibers with a polyester binding agent, resulting in a non-woven mat. Several forms of the cotton fiber were tested to determine which provided optimal sorbent capabilities. The cotton fiber mats were more effective when absorbing various types of hydrocarbons. Gasoline and diesel were absorbed by sorbents maximally, and the sorption was carried out within seconds. Unheated cotton fiber absorbed oil residue to 0.02% (w/w), while heated cotton fiber contained 11.2% residue as compared with 56.1% remaining in the synthetic control mats.

Kapok (*Ceiba pentandra* [L.] Gaertn.) is a natural hollow fibrous material which may serve as a hydrophobic–oleophilic sorbent for oil (Teik and Xiaofeng, 2006). Once the kapok fibers are prepared by removing residues and dried, it is ready for use in its raw form. The hollow and tubular structure of this material (Fig. 1) make it an excellent medium for oil sorption.

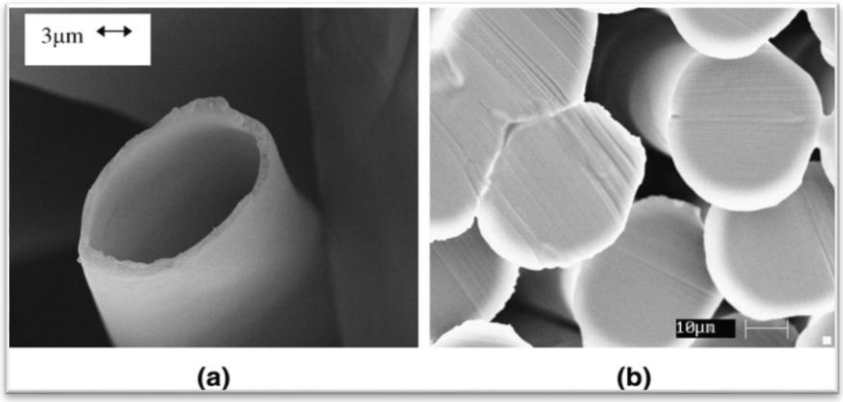

Figure 1. SEM images of the cross-sections of (a) kapok fiber, and (b) polypropylene Fibers (Lim and Huang, 2006).

The hydrocarbon sorption capability of kapok fibers was tested by Teik and Xiaofeng (2006). Different quantities of kapok were placed into steel mesh cells and lowered into a pool of various hydrocarbons. In comparison to other sorbents, kapok was superior in terms of sorption capacity, especially for tightly-packed cells. High packing density was therefore considered necessary for effective sorption. Among the various hydrocarbons tested, diesel was the least absorbed and HD40 was absorbed in greatest quantity. Kapok fibers were more effective once reused compared to polypropylene (PP) fibers; however, PP fibers were still useful for hydrocarbon sorption.

Use of Activated Charcoal as a Sorbent

Activated charcoal, also known as activated carbon, occurs in both granulated and powdered forms. It is commonly used to filter industrial and domestic water by removing toxins through chemical and/or physical sorption processes (Lemley and Wagenet, 1995).

Activated carbon may be produced from materials of vegetable, animal or petrochemical origin (Ferhan, 2014). The annual production of activated carbon is estimated about 100,000 tons worldwide (Krüger, 2010). The basic raw materials used for production of activated carbon include coal (anthracite or brown coal), peat, lignite, wood, nut shells, petroleum coke, coconut shell, and sometimes synthetic polymers. Attempts are also made to utilize agricultural wastes such as biomass residues, rice husks, corn cobs, bagasse, almond, walnut and hazelnut shells (Soleimani and Kaghazchi, 2007) or others such as waste tires, phenol formaldehyde resins, pulp-mill residues, bones, and coffee beans (Cameron Carbon, 2013).

The production of activated carbon involves two key steps: carbonization and activation (Moretto and Woditsch, 2000). Depending on the type of starting organic-rich raw material and carbonization and activation conditions, the properties of the final product will vary significantly.

Activated carbon solids contain pores of different sizes and shapes. According to the definition provided by the International Union of Pure and Applied Chemistry (IUPAC), micropores are pores having a width < 2 nm, mesopores have a width between 2 and 50 nm, and macropores are those having a width > 50 nm. Another classification involves ultramicropores, denoting micropores < 0.7nm (Inglezakis, and Poulopoulos, 2006). As a result of the extensive network of voids (which allow the passage of liquids and vapors), the surface area of activated charcoal ranges from 300-2,000 m^2 g^{-1} (Helmenstine, 2015).

Impurities absorbed by charcoal include chlorine, metals, hydrocarbons, and others. Nitrates, fluoride, and sodium are not filtered as they are not attracted to carbon. According to Helmenstine (2015), activated charcoal needs to be recharged or replaced when the filter becomes saturated (and therefore less effective)

Besides physical characteristics such as particle size, pore structure and surface area, the chemical properties of the carbon surface play an important role in adsorption. The edges and discontinuities in the aromatic sheets in an activated carbon particle are highly reactive locations termed ‘active sites’ or ‘active centers’. These sites interact with different species such as oxygen, hydrogen, nitrogen and sulfur, giving rise to different types of surface groups (Bansal and Goya, 2005). In an activated carbon particle these sites are responsible for surface reactivity, surface reactions, and catalytic reactions (Bansal and Goya, 2005).

Activated carbon surfaces generally contain various oxygen complexes arising from the raw material as well as from chemisorption of oxygen during the activation process. Although, in general, activated carbons are of hydrophobic nature, the presence of oxygen-containing groups on the surface increases the hydrophilicity of activated carbons, since water molecules can form hydrogen bonds with oxygen atoms (Menéndez-Díaz and Martín-Gullón, 2001). Thus, the

chemical structure of an activated carbon type determines its interaction with polar or non-polar adsorbates.

Adsorption is the best-known mechanism for the removal of a species in the presence of activated carbon. Activated carbon can adsorb a wide array of organics and some inorganics, both from the liquid and gaseous phase. Among the organic classes sorbed are aromatics, polynuclear aromatics, chlorinated aromatics, phenolics, high molecular weight hydrocarbons, chlorinated aliphatics, aliphatic and aromatic acids, ketones, esters, ethers and alcohols, surfactants, and soluble organic dyes. Inorganics such as radionuclides and metal ions may also be adsorbed onto activated carbon (Annmäki and Turtianen 2000).

The adsorption of many adsorbates is usually induced by van der Waals forces. This type of adsorption is generally termed physical adsorption or physisorption. In some cases, adsorbates may be removed by chemical adsorption, or chemisorption, where the adsorbate undergoes chemical interaction with activated carbon. The bonds formed between activated carbon and the adsorbate are much stronger in chemisorption compared to physical sorption (Stoltenberg and Pengra, 2012)

Use of Synthetic Materials as Sorbents

Polypropylene fiber sorbents experience high oil sorption capacity but experience reduced uptake of water (Schrader, 1993). Polypropylene fiber is the lightest among fiber sorbents, with a specific gravity of 0.91 (Schmenk et al., 2000), i.e., it floats because it is less dense than water. Consolidated fibrous materials include nonwoven PP sorbents (Fig. 2). These fibrous webs have small holes that allow the movement of liquids into the sorbent material and retain it after sorption (Nederveen, 1994).

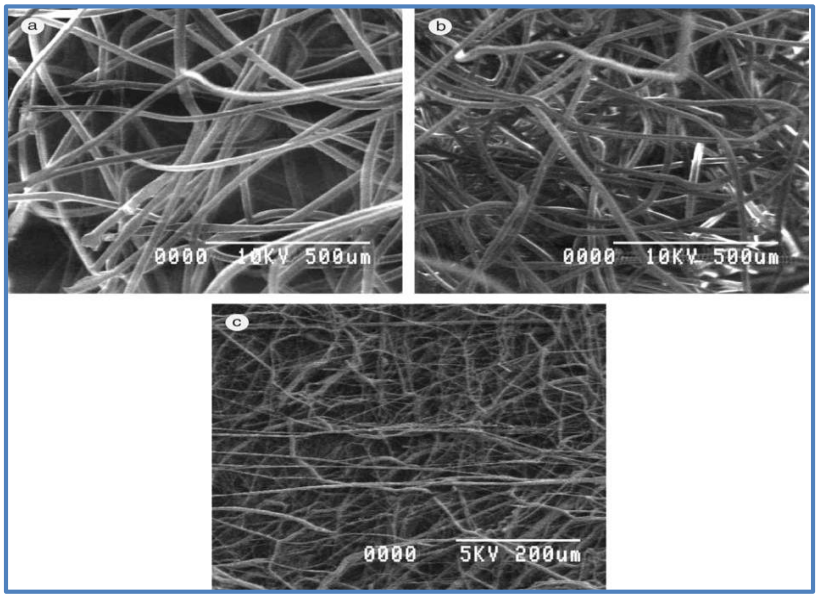

Figure 2. SEM images of non-woven PP oil sorbents: (a) stitch-bonded; (b) needle punched; and (c) melt-Blown (Mather and Fotheringham, 2003).

In a laboratory study, crude oil collected from the North Sea was evaluated in a sorption test (Wei and Mather, 2003). Newly prepared non-woven PP sorbent materials were sliced into pieces and placed in test cells containing a 5-mm layer of oil that was floating on an 80-mm layer of sea water. Oil retention and sorption varied with different sorbents. A high sorption ratio with crude oil was the result of the sorbent having high porosity. Furthermore, oil sorption capacity was correlated to the high viscosity of the oil.

The disadvantages of using sorbent materials for wastewater cleanup are that they: (1) can easily become saturated and sink; (2) are less effective for sorption of fresh light and medium oils; and (3) saturated sorbents are difficult to collect.

Industrial-Scale Systems for Treatment of Drilling Wastewater

Packed Bed Absorption

Packed Bed Absorption technology was designed by ET Ventures in South Carolina. This technology was evaluated in the Rocky Mountain Oilfield Testing Center to determine its effectiveness in adsorbing hydrocarbons from wastewater (Doye et al., 1997). Water from the affected formation was allowed to cool to 90°F and diverted to a three-stage bed adsorption system. The first two stages included a sodium bentonite-modified organo-clay adsorbent. Granular activated carbon (GAC) was present in the final stage (Fig. 3).

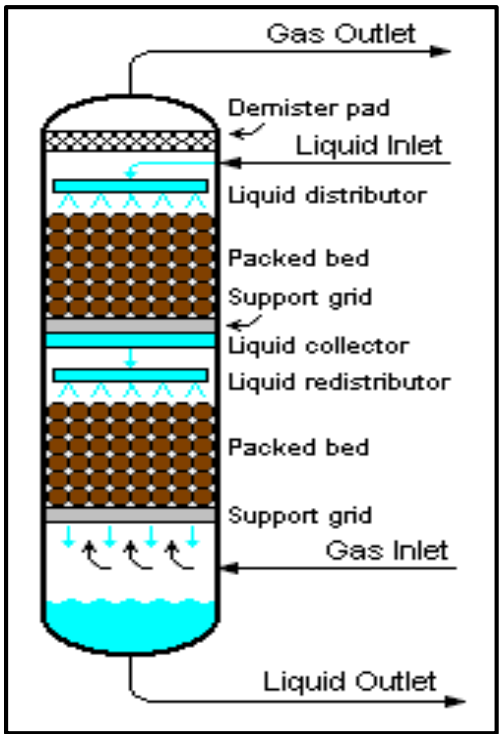

Figure 3. Schematic diagram of a packed bed absorption column (Beychok, 2005).

Table 2. Results from ET Venture mobile produced water treatment system.

Analyte	Before treatment (mg/l)	After treatment (mg/l)
TPH	148	1.1
Oil and grease	151	1.2
Benzene	3.14	< 0.5
Toluene	4.97	< 0.5
Ethylbenzene	4.95	< 0.5
Xylene	29.7	< 1

Source: Doye et al., 1997.

EPA Method EPA 1664 was carried out on samples of inlet feed and effluents from the columns (Table 2). A disadvantage of the system includes the need for the sorbents to be preferentially wetted to avoid reduction of the interfacial area to volume ratio; furthermore, the system cannot handle extremely high or low flow rates.

American Petroleum Institute Separator

The API (American Petroleum Institute) separator was designed to exploit the differences in specific gravity of oil and wastewater (Schultz, 2005). Solids in the wastewater settle to the bottom of the separator as a sediment layer, the oil rises to the top, and the wastewater occurs in the middle layer, i.e., between the oil and solids (Beychok, 1967). The oil layer is skimmed off and the sediment is removed using a chain and flight scraper and sludge pump, respectively (Fig. 4). The water is further treated by dissolved air flotation (DAF) in order to remove any remaining oil. Biological treatment is applied to remove dissolved compounds. Disadvantages of the technology can include: large areas are required for treatment, the system is costly to construct, there is high steam consumption (used in order to avoid freezing of heavier petroleum products), and possible fire hazards exist.

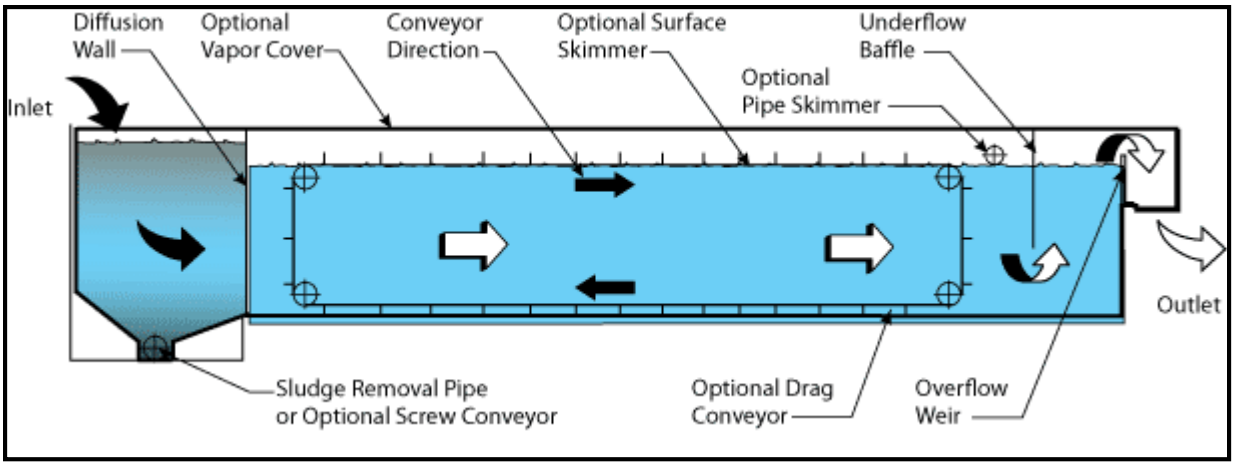

Figure 4. American Petroleum Institute separator (Monroe Environmental, 2016).

Evaporation Processes

Evaporation occurs at the surface of a liquid and involves the conversion of a liquid to a gaseous phase. According to Heins and Peterson (2005), falling film tube evaporators have the largest heat coefficient, which can be used to save energy. Film tube evaporators help reduce fouling by making the tube surfaces wet during operation. The produced water pH is adjusted, the temperature of the produced water is increased, and non-condensed gases are removed when hot liquid is transported to a de-aerator. The vertical tube used in treating wastewater is shown in Fig. 5.

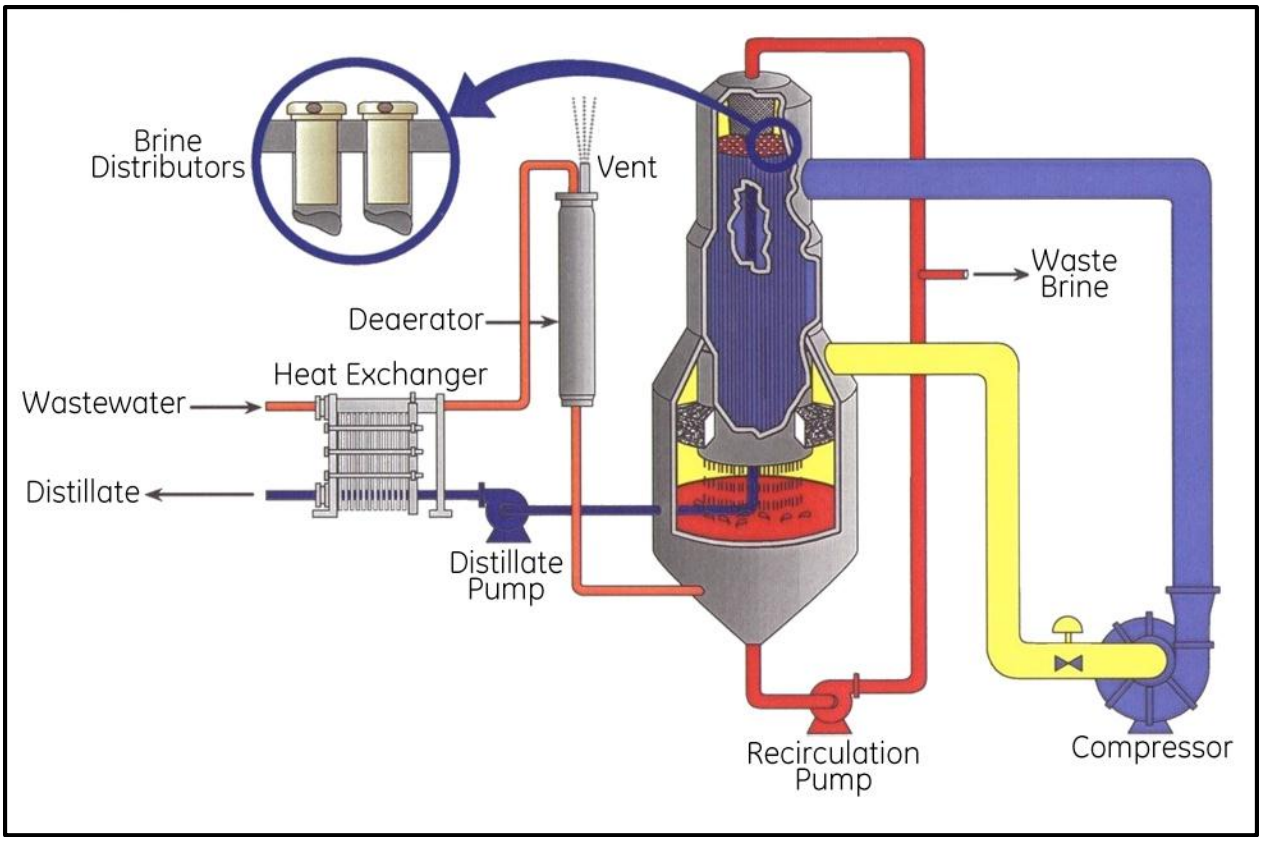

Figure 5. Vertical tube falling film vapor compression evaporator schematic (Ionics Inc.).

Hot de-aerated brine is transferred through a sump and thereby joins with recirculating brine slurry. "The slurry is pumped to the top of a bundle of heat transfer tubes and flows down into each tube through a liquid distributor" (Heins and Peterson, 2005). At the end of the system, the vapor condenses as clean water, and is pumped back with the help of a heat exchanger. High inputs of energy are required for heating the air. In addition, the handling of significant quantities of solids is a disadvantage of this technology.

Rapid Spray Evaporation (RSE)

The Rapid Spray Evaporation (RSE) technology was developed by Aqua Sonics Corporation in Albuquerque, NM. This system treats contaminated water via utilization of a specialized nozzle combined with use of waste heat. Air is blown into an evaporation chamber

equipped with a heating element. As the heated air flows through the chamber, nebulized wastewater is forced in. Brine droplets and vapor flow through a mechanical filter which retains the brine. When the water vaporizes, the solids present in the solution separate. The vaporized water is then condensed and collected via a vacuum process; solids are a byproduct. The technology is effective for removal of dissolved solids and various salts (Table 3) (Daniel and Bruce, 2005). One of the disadvantages of RSE technology is that large quantities of energy are required for heating air and the handling of solids.

Table 3. Results of wastewater treatment via RSE technology.

Solute	Untreated wastewater (mg/l)	Treated wastewater (mg/l)	Concentrate (mg/l)
Calcium	79	1.6	20
Magnesium	490	1.7	600
Sodium	25,000	160	57,000
Potassium	610	1.9	1,100
Chloride	5,000	90	8,400
Sulfate	31,000	150	35,000
Bicarbonate	5,700	20	2,900
Phosphate	1,200	0	-
Carbon dioxide	3,100	0	-
Total dissolved solids	130,000	440	180,000

Source: WestWater Resource Inc., NM.

Freeze Thaw Evaporation (FTE)

The FTE process involves storing a large volume of water (i.e., pond size) where it will be chilled to temperatures below freezing. The cold water is transferred to a location where it will be sprayed onto pipes to freeze. Through ‘conductivity-controlled valves’ the water is

separated into brine and fresh water. This brine is removed to return to the FTE process or disposed. The remaining frozen product consists of fresh water that is safe for multiple purposes including human consumption and agriculture (Boysen, 2007).

Another way to achieve FTE, other than using the 'spray freezing' technique, involves retaining the pond water in its original reservoir and allowing it to completely freeze. In this situation the brine forms below the ice and is removed; therefore, the remaining ice is mostly purified water upon melting.

The disadvantages of FTE technology are that it requires a local climate with temperatures below the freezing point; it requires large tracts of land, (i.e., about 35 acres for a 1000 bbl facility); and it requires a long operational cycle (Boysen, 2007).

Pressure-Driven Membrane Separation Technologies

Pressure-driven membrane separation technologies are among the most common industrial-scale processes used for water purification. Several techniques may be involved, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and gas liquid membranes. These processes work by applying high pressure across a membrane, resulting in various impurities being physically and/or chemically filtered out, leaving the remaining water in a relatively pure state.

Pressure-driven membrane separation technologies are being improved by perfecting the membranes for maximum removal efficiency. Although these processes are effective, removal of all dissolved species is not yet feasible, as membranes reject various species based on molecular weight (Daniel and Bruce, 2005).

Although pressure-driven membrane separation technologies are the most common methods for water treatment, there are several drawbacks to their utilization. For instance,

membrane fouling can result from residues like oils and other agents adhering; in addition, filtration will fail due to tears in the membranes caused by the high system pressure. These concerns underscore the importance of designing a membrane that is sufficiently permeable to eliminate species of all sizes and sturdy enough to withstand extremely high pressures to prevent shearing (Daniel and Bruce, 2005).

Oxidation Processes

Chemical oxidation is a treatment process for removal of sulfur, manganese, iron, color, odor, and synthetic organic chemicals from water. The overall process includes two half-reactions, i.e., a reduction reaction where an atom or molecule gains electrons, and an oxidation reaction where a molecule donates electrons (AWWA, 2005). Some of the common oxidants used in water treatment are chlorine, chlorine dioxide, permanganate, oxygen, and ozone. According to AWWA (2005), the quantity of oxidant to apply depends on factors such as the quality of raw water, types and quantities of contaminants present, and power costs.

Oxidation treatment of industrial wastewater is reliable and requires minimal equipment (Bureau of Reclamation, 2003). Application of oxidizing chemicals requires a sufficient time of contact between oxidants and water. Pretreatment is often not required; however, removal of oxidized particles requires solids separation and post-treatment. Equipment is needed to generate the oxidant on-site.

One of the disadvantages of oxidation technology is that the cost of chemicals may be significant. In addition, chemicals employed may be corrosive and/or explosive; therefore, workers using oxidation technology must be properly trained in its use. Table 4 provides an overall assessment of oxidation technologies.

Table 4. Assessment of oxidation technology for wastewater treatment.

Criteria	Description/Rationale
Industrial status	A reliable and well established technology. Minimal equipment is required to remove BOD, COD, organic and inorganic compounds like iron and manganese.
Feed water quality	High removal of divalent and monovalent ions, organics and metals.
Product water quality	Depends on oxidant used.
Production efficiency (recovery)	Recovery is 100%.
Infrastructure considerations	Requires chemical metering.
Energy consumption	Approximately 18% of the total operations and maintenance (O&M) costs of oxidation processes.
Chemicals	Many oxidants are hazardous to human health. Adequate training in their use is required. The cost of chemicals may be high.
Life cycle	Chemical metering pumps are critical components of the oxidation system. The life span of chemical metering equipment can be 10 years or greater.
O&M considerations	It is required to maintain chemical meter pumps and to conduct periodic calibration.
Overall costs	O&M costs are unknown; capital costs can be $ 4.7/gpd.
Pre-and post-treatment	Pre-treatment is not required for oxidation. Post-treatment may involve management of residuals, e.g., solids. It may be necessary to capture and/or treat vapors released from the system.
Concentrate management or waste disposal	Waste is produced from oxidation processes. The waste should be tested to determine whether or not it is hazardous, and must be managed accordingly.

Source: Colorado School of Mines, 2009.

Oxidation Reactor

An oxidation reactor was initiated by New Park Environmental Services for treating petroleum wastewater. This technology is based on aggressive oxidation and precipitation of contaminants. The chemical/physical treatment stage of the technology is the HB Reactor (sonic oxidation). The chemical/physical stage is often adequate to achieve many water treatment requirements. Contaminants that are already dissolved, such as monovalent salts, are resistant to oxidation/precipitation and may not be removed during this stage. However, in the demineralization stage they can be removed. The disadvantage of the technology is that an on-site supply of oxidizer is required; additionally, there are requirements for separation of precipitate (Katie and Katharine, 2011).

Constructed Wetlands for Treatment of Hydraulic Fracturing Fluids

The concept of using constructed wetlands for treatment of municipal and industrial wastewaters originated early in the 20th century (Vymazal and Kropfelova, 2008). Constructed wetlands are used to improve the quality of point and nonpoint sources of water pollution including storm water runoff, domestic wastewater, agricultural wastewater, and coal mine drainage. Constructed wetlands are also used to treat petroleum refinery wastes, compost and landfill leachates, fish pond discharges, and pretreated industrial wastewaters, such as those from pulp and paper mills, textile mills, and seafood processing. For some wastewaters, constructed wetlands are the sole treatment; for others, they are one component in a sequence of treatment processes (United State Department of Agriculture-Natural Resources Conservation Services, 2015).

Types of constructed wetlands

Natural systems for wastewater treatment cover a wide range and are classified into three categories according to their location in the landscape and the saturation state of the soil: (1) upland or terrestrial systems, (2) wetland systems and (3) deeply flooded or aquatic systems. Aquatic systems are open-water, pond-like systems that are dominated by algae or floating, submerged or emergent plant species. In terrestrial systems, the unsaturated soil has a dual role, first serving as a filtration medium for pollutant removal and secondly functioning as a rooting medium for plant growth. The major terrestrial systems are on-site infiltration and low and high rate land systems (Kadlec and Knight, 1996). Wetlands, which are the transitional areas between terrestrial and aquatic ecosystems, are inundated during the whole or part of the year and are dominated by vegetation adapted to these waterlogged conditions (Price and Probert, 1997).

Constructed wetlands (CWs) are designed to provide wastewater treatment and are the engineered equivalent of their natural version. They are man-made wetlands constructed in areas where they do not naturally occur. Wetlands can provide additional benefits such as creation of controlled flooding areas, creation of habitats for fauna and flora, food production, recreational use, etc. (Sundaravadivel and Vigneswaran, 2001). Constructed wetlands that are used for primary and secondary wastewater treatment are often called constructed treatment wetlands, whereas constructed wetlands which provide advanced treatment of secondary treated wastewater and other benefits such as wildlife habitat and recreational use are often called enhancement wetlands (EPA, 2000).

Constructed wetlands are classified into the following different types according to the water flow mode and the dominant aquatic plant species (Kadlec et al., 2000) (Fig 5):

1. Free-Water-Surface (FWS) Constructed Wetlands consist of shallow basins that are provided with a liner or a layer of clay to prevent contamination of the groundwater. A layer of soil or sediment supports growth of rooted macrophytes. The wastewater is directed horizontally through a dense mass of aquatic macrophytes. Water flow is above ground; systems are categorized into the following subtypes according to the dominant plant species (Lesage, 2006):

- Emergent aquatic macrophytes or helophytes: rooted in a substrate or floating in a mat; e.g. *Phragmites australis*, *Typha* spp., *Juncus* spp., *Carex* spp., etc.
- Floating aquatic macrophytes or pleustophytes: floating-leaved, bottom-rooted; e.g. *Nymphaea* spp., *Nelumbo* spp., etc., or free-floating; e.g. *Eichhornia crassipes*, *Lemna* spp., etc.
- Submerged aquatic macrophytes or hydrophytes: e.g. *Elodea* spp., *Myriophyllum* spp., *Potamogeton* spp., etc.

2. Subsurface Flow (SSF) Constructed Wetlands: with the water flow below ground.

Horizontal subsurface flow CWs consist of shallow basins provided with a liner and filled with a granular medium such as gravel or sand, or even soil. Coarse gravel is often used in the inlet and outlet area to obtain optimum flow distribution. A drainage tube at the bottom of the outlet area allows the evacuation of effluent. Vertical subsurface flow CWs consist of one or more layers of a granular medium such as coarse sand and/or gravel, or soil. SSF CWs are categorized into the following subtypes according to the water current direction:

- Horizontal SSF: planted with helophytes; e.g. *Phragmites australis*, *Juncus* spp., etc.
- Vertical SSF: planted with helophytes; e.g. *Phragmites australis*, *Juncus* spp., etc.

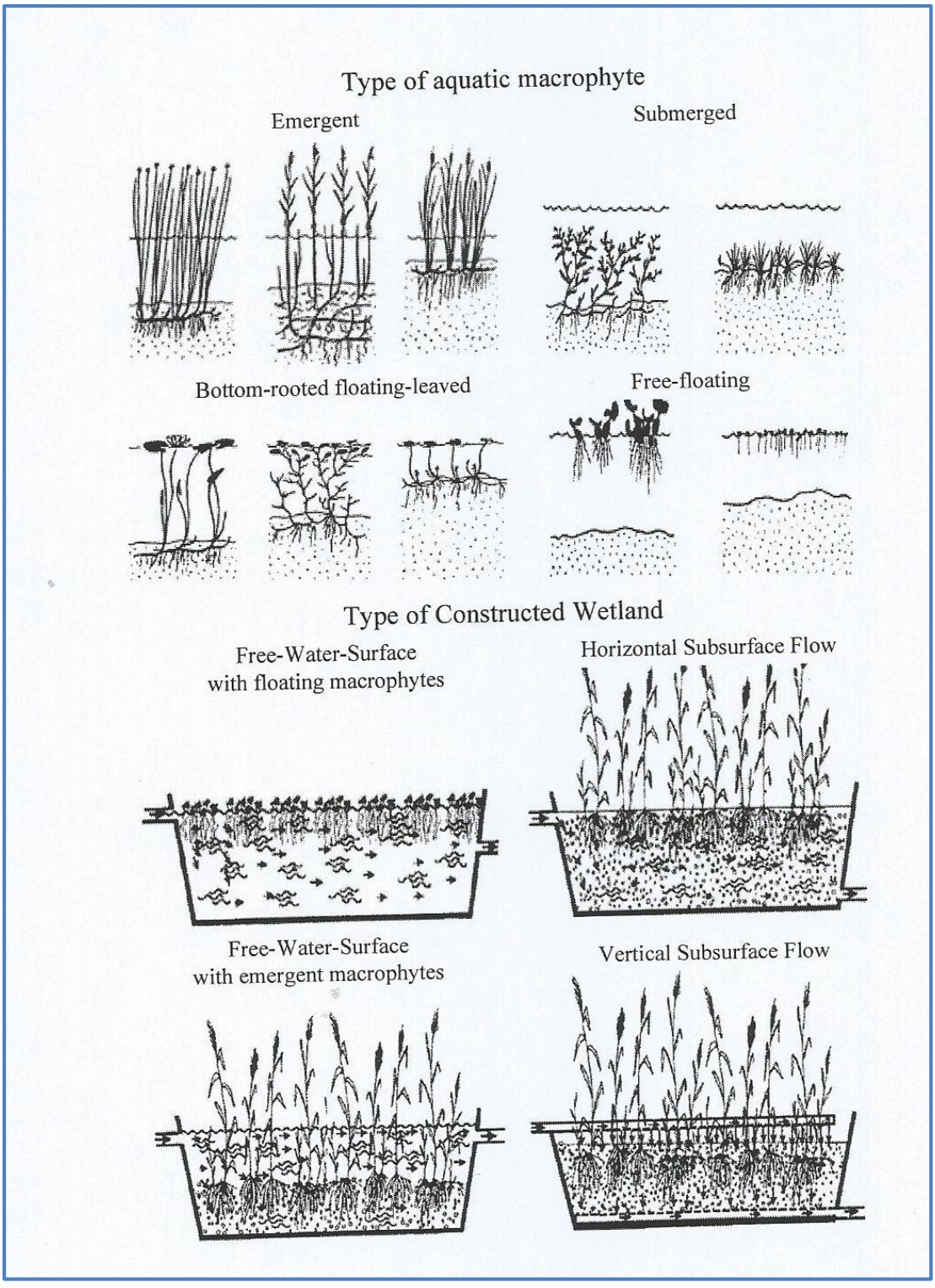

Figure 6. Types of constructed wetlands (Lesage, 2006).

Constructed wetlands are designed to treat dissolved and suspended wastewater contaminants using plants in aqueous ecosystems. Most wetlands support a dense growth of vascular plants adapted to saturated conditions. This vegetation slows the flow of water, creates microenvironments within the water column, and provides attachment sites for microbial communities. The litter that accumulates as plants die back in the autumn creates additional material and exchange sites, and provides a source of carbon, nitrogen, and phosphorous to fuel microbial processes (USDA-NRCS, 2015). Wetland construction is inexpensive and has low operational costs. Benefits accrue for the environment, aesthetics, wildlife and livestock (Kuipers, 2004).

A key component of constructed wetlands is that their functions are largely regulated by microorganisms and their metabolism (Wetzel, 1993). Bacteria, yeasts, fungi, protozoa, and algae are all considered to be essential microorganisms in treatment of wastewater in constructed wetlands. Many organic carbon compounds are broken down (i.e., mineralized) and nutrients are subsequently released via microbial processes. This microbial activity involves breaking down both inorganic and organic substances into soluble phases via either aerobic or anaerobic mechanisms. Microbial activity also changes the oxidation and reduction environment of the substrate, which results in the altering of the wetland processing capacity along with the nutrient recycling system.

The environment of the microbial community changes in regards to the water supply and chemical conditions of the water. The presence of energy-rich substances helps to increase microbial populations rapidly. However, when the environmental conditions are not favorable they no longer thrive; microbial cells actually become dormant, which can last for years (Hilton, 1993). The presence of toxins in a wetland significantly threatens the microbial population.

Some of these threats include heavy metals and pesticides; therefore, it is necessary to ensure these chemicals are prevented from being introduced to the microbial communities in high quantities.

Constructed wetlands are usually planted with emergent vegetation (non-woody plants that grow with their roots in the substrate and their stems and leaves emerging from the water surface). Common emergents used in constructed wetlands include bulrushes, cattails, reeds, and a number of broad-leaved species.

Vascular plants contribute to the treatment of wastewater and runoff in a number of ways. For instance, they stabilize substrates and limit channelized flow; they slow water velocities, which allows suspended materials to settle; they take up carbon, nutrients, and trace elements and incorporate them into plant tissues; they transfer gases between the atmosphere and the sediments; leakage of oxygen from subsurface plant structures creates oxygenated microsites within the substrate; plant stem and root systems provide sites for microbial attachment; and plants create litter, high in organic matter content, when they die and decay (USDA-NRCS, 2015).

Typha latifolia

Some aquatic plants have been documented with the ability to remove nutrients (Rogers et al., 1991; Moshiri, 1993; Mungur et al., 1997; Gottschall et al., 2007; Chung et al., 2008) and heavy metals (Deng et al., 2004; Miretzky et al., 2004; Maine et al., 2006; Upadhyay et al., 2007) from aquatic environments. Many scientists have focused on accumulation of heavy metals by aquatic macrophytes (Manios et al., 2003; Espinoza-Quinones et al., 2005; Saygideger and Dogan, 2005; Fritioff and Greger, 2006; Skinner et al., 2007; Licina et al., 2007). In addition, some have studied the phytoremediation of aquatic macrophytes for contaminated

sediment and aquatic environments (Hinchman et al., 1998; Osmolovskaya and Kurilenko, 2001; Panich-Pat et al., 2004; Gratao et al., 2005; Audet and Charest, 2007).

Among aquatic macrophytes, *Typha latifolia* L. is a common wetland plant that grows widely in temperate and well as tropical regions (Ye et al., 1997). *Typha latifolia* L. has a high capacity for taking up and incorporating heavy metals (Mc Naughton et al., 1974). Pip and Stepaniuk (1992) investigated some aquatic plants as pollution indicators due to their abilities to absorb and tolerate heavy metals. *Typha* tolerates enhanced levels of metals in its tissue without serious physiological damage. Dunbabin and Bowmer (2002) reported metal concentrations to increase in the following order: roots > rhizomes > non-green leaf > green leaf. They reported that metal uptake by plants was highest in the roots in contaminated cases, and the green leaves have lowest concentrations in Cd, Cu, Pb and Zn. The concentration of heavy metals in the tissue of cattails (*Typha* spp) is highly dependent on a number of parameters, like the solution pH, the original heavy metals concentration in both the solution and the substrate and the exposure time (Karathanasis and Thompson, 1993).

Artificial wetlands may be constructed in order to treat oil field produced water (Xiang and Yue, 2010). A constructed wetland was able to reduce Fe and Ba concentrations after six months of operation (Coffey, 2016). There was, however, an increase in sodium adsorption ratio (SAR) from 12 to 14.1 (Bauder, 2002).

Hypothesis and Objectives

The objective of the reported research was to determine the effectiveness of two techniques for treating hydraulic fracturing fluids (fracking fluids) for possible re-use by oil and gas industries.

Specifically, the objectives were to:

1. Evaluate the ability of shredded plastic, cationic exchange resin, granular activated charcoal, and peat in sorption of heavy metals from fracking fluid.

2. Evaluate the ability of *Typha latifolia,* grown in a constructed wetland, in ameliorating pH and electrical conductivity, and in sorption of heavy metals from fracking fluid.

3. To assess the ability of *Typha latifolia* for uptake and accumulation of Na, Cu and Pb for possible phytoextraction purposes.

Research Hypotheses:

1. Peat and cationic exchange resin will provide greater sorption of heavy metals (Cu and Pb) compared with shredded plastic due to the greater number of charged sites per unit weight.

2. Constructed wetlands will improve pH of the fracking fluid due to its high pH and strong buffering capacity.

3. *Typha latifolia* will effectively remove Na, Cu, and Pb from flacking fluid.

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CHAPTER 2: EXPERIMENTAL METHODS

Column Study

Simulated hydraulic fracking fluid (HFF) was prepared in the laboratory and pumped through selected materials packed in columns to determine relative sorption capabilities. Sorbents included activated charcoal, synthetic resin, shredded plastic, and peat. The charcoal was purchased from Grainger (Muncie, IN). The synthetic resin (Dowex G-26™) was purchased from SigmaAldrich. The shredded plastic was received from Hoehn Plastic (Poseyville, IN). Peat was purchased from a local commercial supplier. The sorbents were packed into PVC tubes measuring 5 cm inner diameter and 30 cm in length. Density of the material in each column was approximately 10 g/cm^3.

Pore volume was determined after estimation of bulk density and porosity. One pore volume was equal to the entire pore space of a single packed column.

Test Fluids

A synthetic hydraulic fracking fluid (HFF) was prepared. The chemical composition was based on data from Marcellus and BF Environmental (2016).

Table 5. Chemical composition of the simulated hydraulic fracturing fluid.

Chemical	Quantity
Acetic acid	10 ml
Acetone	10 ml
Aluminum chloride	10 ml
Ammonia	10 ml
Ammonium acetate	10 ml
Ammonium chloride	10 ml
Ammonium fluoride	10 ml
Ammonium nitrate	10 ml
Boric acid	10 ml
Butanol	10 ml
Citric acid	10 ml
Copper sulfate	10 g
Ethanol (ethyl alcohol)	200 ml
Ethylene glycol	5 ml
Glycerol	10 ml
Hexane	10 g
Hydrochloric acid	10 ml
Hydroxylamine hydrochloride	10 g
Lead pellets	10 g
Magnesium carbonate	10 g
Magnesium chloride	10 g
Magnesium nitrate	10 g
Methanol (methyl alcohol)	200 ml
Phosphoric acid	100 ml
Potassium acetate	10 g
Potassium chloride	10 g
2-propanol	10 ml
Sodium acetate	10 g
Sodium carbonate	10 g
Sodium chloride	10 g
Sodium hydroxide	10 g
Sodium silicate	10 g
Toluene	10 ml
Diesel fuel	10 ml

Adapted from: Marcellus and BF Environmental (2016).

Each HFF was pumped through the respective columns (26 replications each) using a Masterflex™ peristaltic pump (Fig. 13). The liquids were pumped at a rate of 5 ml/min. Liquids were collected at 24, 48, 72 and 96 hours and stored at 4^{o}C until analyzed.

Figure 7. Column setup for pumping of fracking fluid (author).

Determination of Chemical Properties of HFF Leachates

Leachates from each column were tested for specific conductivity using a hand-held conductivity meter (Oakton, Vernon Hills, IL); pH was measured using an Oakton glass electrode pH meter. Volatile organic compounds were assessed using a Varian photoionization detector.

Leachates were filtered using Whatman no. 42 filter paper to remove sediment. Filtered samples were tested for sodium (Na), potassium (K), magnesium (Mg), copper (Cu), and lead (Pb) using flame atomic absorption spectrophotometry (FAAS) with a Varian 2000 Perkin Elmer instrument. Standards were checked after running every 5 samples.

Determination of Leachate Toxicity

The Muta-chromo ™ system was used to determine potential toxicity of the leachates exiting the columns. The system was purchased from Environmental Bio-detection Company, Ontario, Canada.

Nutrient broth was prepared and mixed with a culture of lyophilized bacteria. The mixture was incubated at 37 °C for 16-18 h. A 5 µl bacterial suspension was removed from the culture and added to sterilized glass test tubes. Contents were transferred to a multi-channel pipette reagent boat. Aliquots of 200 µl were poured into wells of a 96-well micro-titration plate using a sterile micropipette. The plate was covered with a lid and sealed to prevent evaporation. Plates were incubated in an air-tight plastic bag for 3-6 d at 37°C. Plates were removed from the incubator and scored on the basis on production of color.

Constructed Wetland Study

Simulated constructed wetlands (C W) were established in the Ball State University greenhouses. The system contained 20-liter plastic trays, measuring 10 cm tall, 40 cm in length, and 15 cm width. Each container was filled with 10 kg of Glynwood soil (fine, illitic mesic Aquic Hapludalf, obtained from an agricultural field in Delaware County, Indiana) which had first been sieved to pass a 2-mm mesh sieve.

The treatment system included two trays (‘Stage 1’ and ‘Stage 2’) in series (Fig. 15). The trays were planted with cattail (*Typha latifolia*); a total of 15 plants were placed in each tray. The plants were collected from a Ball State University wetland located in Muncie, IN. There were three replications of this treatment. *Typha latifolia*, is a species widely used in CW systems due to its high yield, non-invasive characteristics and resilience (Brisson and Chazarenc, 2009).

Two control systems were established: One control contained two trays in series, grown to *Typha*, which received tap water only; the second control received HFF but was devoid of vegetation.

Soil properties were determined as follows. Soil pH was analyzed using a glass electrode pH meter (Accumet® AP115, USA); organic matter was determined via the Walkley-Black titration method (Walkley and Black, 1934) and soil texture by the hydrometer method (Allen et al., 1974). Electrical conductivity was determined using an EC meter (Hanna instruments HI 993310, USA), 26 total N via the Kjeldahl method (Black 1965), extractable P via the Bray II method (Bray and Kurtz, 1945), and extractable K via atomic absorption spectrophotometry after NH_4OAC extraction (Sparks, 1996). Total and extractable metal (Cu, Cr, Pb) concentrations were determined by flame atomic absorption spectrophotometry (FAAS; AAnalyst 200, PerkinElmer®).

Harvested plant material was oven-dried at 80°C for 4 days and the dry weight was recorded. Dried plant material was cut into small pieces with stainless steel scissors. One-half gram (d.w.) of plant material was transferred to a vessel tube for acid digestion [conc. 70% nitric acid (HNO3)], using a MARS microwave digestion apparatus (CEM Corporation, Matthews, NC) and analyzed with FAAS.

Liquids exiting the end tray for each treatment were collected after 30 d. The liquids were brought to the laboratory and analyzed for pH, EC, and concentrations of Cu, Cr and Pb using the methods described above.

Several parameters were calculated to determine metal uptake by *Typha*. The translocation factor (TF) for each plant was calculated by dividing metal concentration in the shoot by metal concentration in the root. A TF value >1 indicates the plant's potential to

translocate metal effectively from root to shoot (Rezvani and Zaefarian, 2011). The equations are as follows:

$TF_{leaf} = C_{leaf}/C_{root}$

$TF_{stem} = C_{stem}/C_{root}$

where C_{leaf}, C_{stem} and C_{root} are the metal concentrations in leaf, stem and root, respectively.

The bioconcentration factor (BCF) is defined as the ratio of metal concentration in the shoot to the extractable metal concentration in the rhizosphere soil (Rezvani and Zaefarian, 2011). This value reflects the progressive accumulation of metal in the plant (Branquinho et al., 2007). The bioconcentration factor for metals was calculated as follows:

$BCF_{leaf} = C_{leaf}/C_{soil}$ (extractable metal)

$BCF_{root} = C_{root}/C_{soil}$ (extractable metal)

where C_{leaf} and C_{root} are the metal concentrations in leaf, stem and root, respectively, and Csoil is the metal concentration in the sediment.

Metal uptake indicates metal concentration in the plant tissue, which is sequestered via the root system (Meeinkuirt et al. 2016):

M uptake = $M_{shoot\ root}$ x Plant dry biomass

where M is the concentration of M in the plant part (shoot or root).

Statistical Analyses

All data obtained for properties of the HFF as a function of treatment, both in in the column study and the constructed wetland study, were tested for statistical significance using three-way analysis of variance (ANOVA). Data showing significance at $\alpha = 0.05$ were analyzed using a

Pairwise Comparisons Test. SPSS™ and MS Excel™ were used on a Windows-based PC for all statistical analyses.

Fig. 8. The constructed wetland system included two trays in series with three replications (author).

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CHAPTER 3: RESULTS AND DISCUSSION

Properties of Hydraulic Fracturing Fluid

The synthetic fracking fluid had a pH of 4.15 and an EC of 275.9 dS/m (Table 6). Concentrations of Pb and Cu were 4.1 and 4.4 mg L^{-1} respectively. Concentrations of Na, K and Mg were 4.7, 4.8 and 4.4 mg L^{-1}, respectively. These levels of metals and other parameters for the synthetic fracking fluid are similar, in some respects, to those provided in the published literature. For example, Igunnu and Chen (2012) measured pH of 4.3 in oil field produced water. In contrast, however, ALL (2006) noted a pH of 8.1. Igunnu and Chen (2012) measured an EC of 4200 uS/cm in fracking fluid and Na concentrations ranged from 132-97000 mg L^{-1}. The same authors found K concentrations to range from 24-4300 mg L^{-1}, Mg from 8-6000 mg L^{-1}, Cu from < 0.02 to 1.5 mg L^{-1}, and Pb from 0.002 to 8.8 mg L^{-1}. ALL (2006) measured Na, K and Mg levels of 486, 13.5 and 13.2 mg L^{-1}, respectively. Such variations in pH (and in other analyte concentrations) are quite common, however, given the wide range of recipes used in preparing hydraulic fracturing fluids.

Table 6. Chemical composition of synthetic hydraulic fracturing fluid (HFF).

Parameter	Value
pH	4.5
EC (dS/m^{-1})	22.1
Na, mg L^{-1}	4.66
K, mg L^{-1}	4.82
Mg, mg L^{-1}	4.35
Cu, mg L^{-1}	4.35
Pb, mg L^{-1}	4.12

Column Study

The pH of leachates from the columns ranged from 6.02 (plastic, 10 pore volumes) to 7.41 (GAC, 50 p.v.) (Fig. 9). The pH of hydraulic fracking fluid before passing through the sorbents was 4.14. The pH of the GAC sorbent was 9.4 (data not shown). Coconut shell based-activated carbon normally is specified for a pH of 9-11 (Indo-German, 2016). Activated carbon can experience pH and alkalinity spikes of significant duration when used for water treatment (Desotec, 2016). The pH increase and duration are dependent on the type of activated carbon and the chemical composition of the water.

The pH value of the peat sorbent was 4.96 (Data not shown). pH values for peat vary widely. Peat is often very acidic (pH < 4.5) (Waikato, 2016); however, Gundogan et al. (2003) measured a pH value for peat of 7.65.

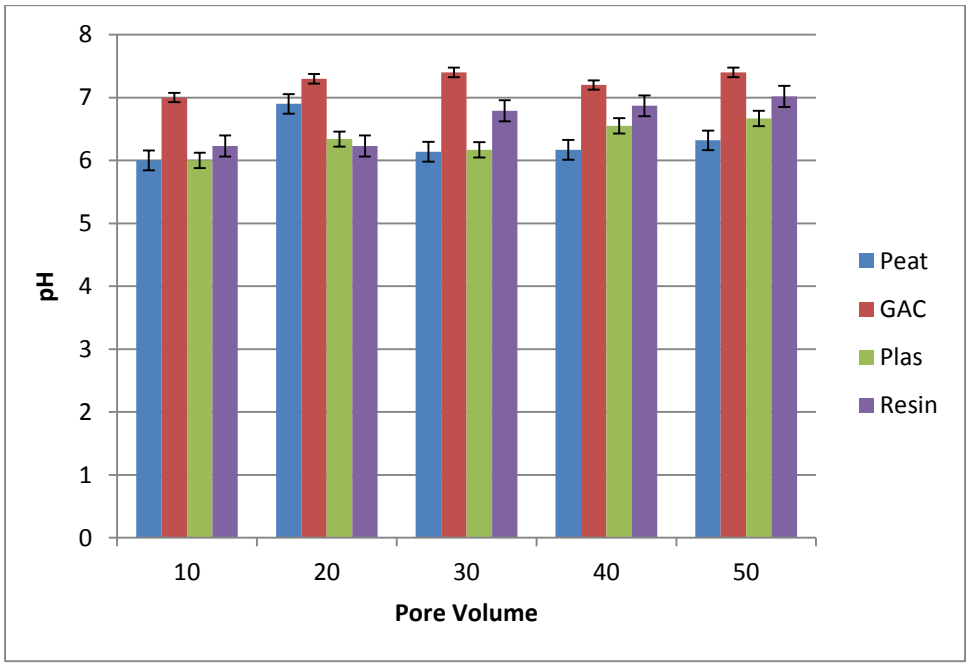

Figure 9. pH of CW effluent as a function of treatment.

Leachate EC values ranged from 12.15 (GAC, 40 pv) to 24.3 dS/m (peat, 30 pv) (Fig. 10). These values compare with 22.1 dS/m for the raw fracking fluid.

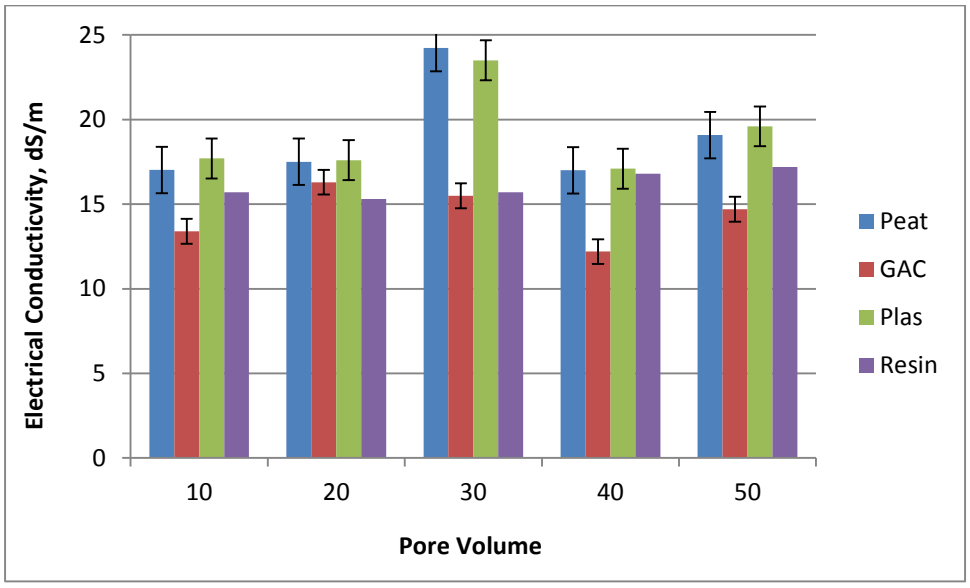

Figure 10. Electrical conductivity of CW effluent as a function of treatment.

The GAC provided the greatest removal of Na from the HFF (Fig. 11) – at 10 pv, 80% removal was observed. Removal declined steadily to 65% removal by 50 pv. Peat was second in efficiency of Na removal, ranging from 32 to 41% (Fig. 3). Both sorbents are known to have a high exchange capacity. Among 64 peat samples from Canada, CEC ranged from 108 to 162 $cmol \cdot kg^{-1}$ (Rippy and Nelson, 2007). The Dowex resin provided the lowest Na recovery, ranging from 4 to 19%. This result was unexpected, as Dowex cation exchange resins are widely

used to remove sodium from water (Dow, n.d.). According to the vendor website, use of this resin resulted in a decrease in Na concentrations from 486 down to 12 mg/l (Dow, n.d.).

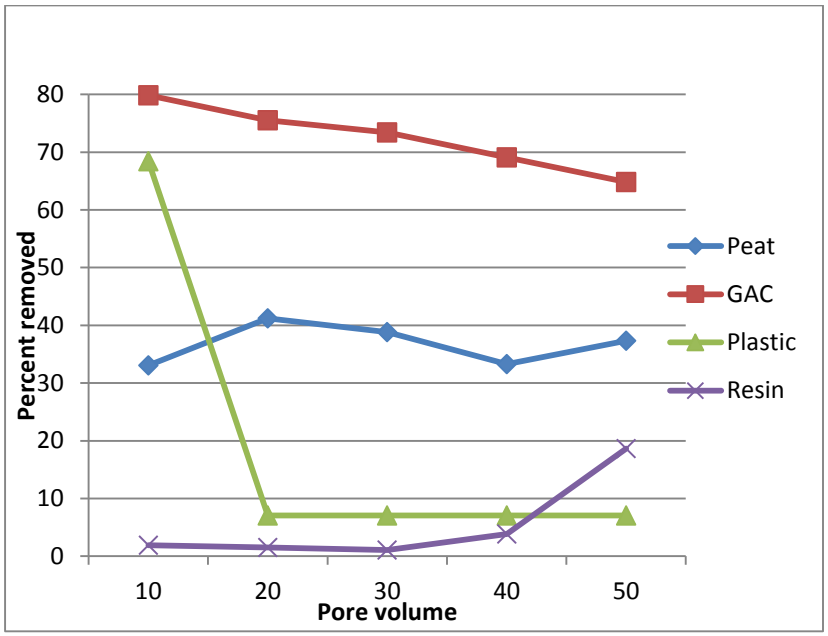

Figure 11. Percent removal of Na as a function of treatment.

The trend of K removal from the HFF was very similar to that for Na removal (Fig. 12): GAC provided the greatest removal. At 10 pv, 82% removal was noted, which increased to 100% removal at 20 pv. Removal declined to 80% removal by 50 pv. The peat was second in efficiency of K removal, ranging from 69% (20 pv) to 72% (40 pv) (Fig. 4). The Dowex resin provided the least K recovery, ranging from 2 to 19%.

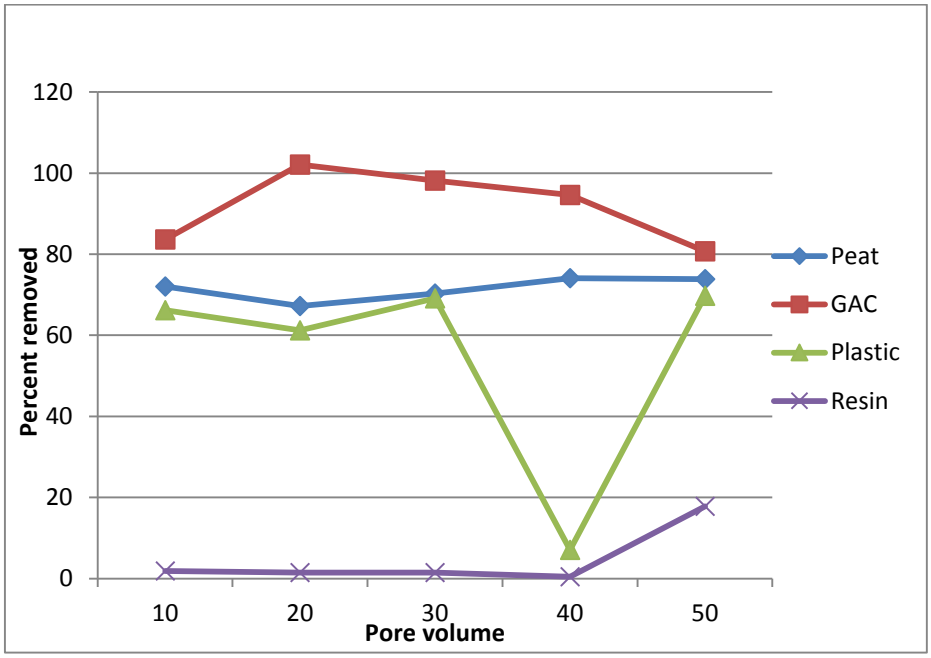

Figure 12. Percent removal of K as a function of treatment.

Magnesium recovery was highly variable, depending on treatment and pore volume (Fig. 13). Maximum removal occurred with the GAC (92%) at 20 pv. Removal with GAC declined sharply and then increased to 50% at 40 pv. The plastic treatment resulted in Mg removal ranging from 35% (20 pv) to 77% (30 pv). This is considered unusual, as the plastic is not expected to have a significant exchange capacity.

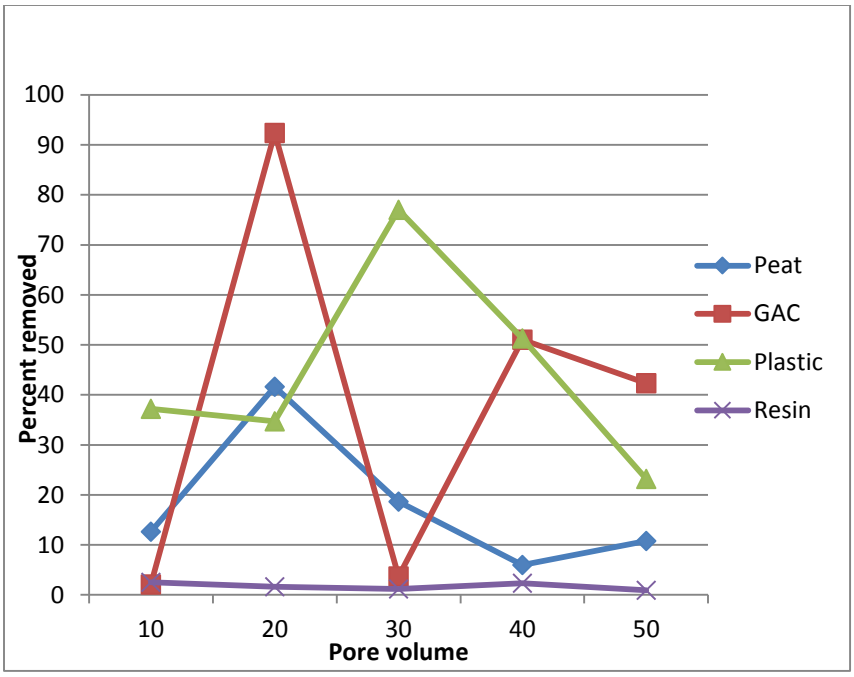

Figure 13. Percent removal of Mg as a function of treatment.

The GAC treatment adsorbed the most Cu of all treatments, ranging from 92% (20 pv) to 50% (40 pv) (Fig. 14). The greater number of surface functional groups available in GAC results in a higher amount of Cu that will be absorbed (Nasim et. al., 2003). Herbert et al. (2012) determined the CEC of activated charcoal to range from 22.2 to138.5 cmol/kg. Mohamed (2009) found that activated carbon sorbed 99% of added Cu. Activated carbon was able to remove Cu more effectively at pH 6 compared to pH 5 (Mohamed, 2009). This is likely due to a tendency of Cu (and other transition metals) to precipitate as oxides and hydroxides as pH increases (Sposito, 1979). Removal of metals using activated charcoal is common in a number of industrial processes (Goel and Kadirvelu, 2005).

Little Cu was sorbed by peat. This was considered unusual, as peat contains a wide range of reactive functional groups. Peat has been found effective with regards to adsorption of metals,

by virtue of the presence of carboxylic, hydroxyl and phenolic functional groups (Lens et al., 1994; Pal et al., 2014).

Essentially no Cu sorption was detected in the plastic treatment (Fig. 14). The lack of effect was expected, as the plastic is not expected to have many charged sites. Adsorption of metal ions from solution is influenced by type of sorbent as well as pH, concentration of sorbent, sorbent properties, and amount of co-ions in the solution (Paliulis, 2014).

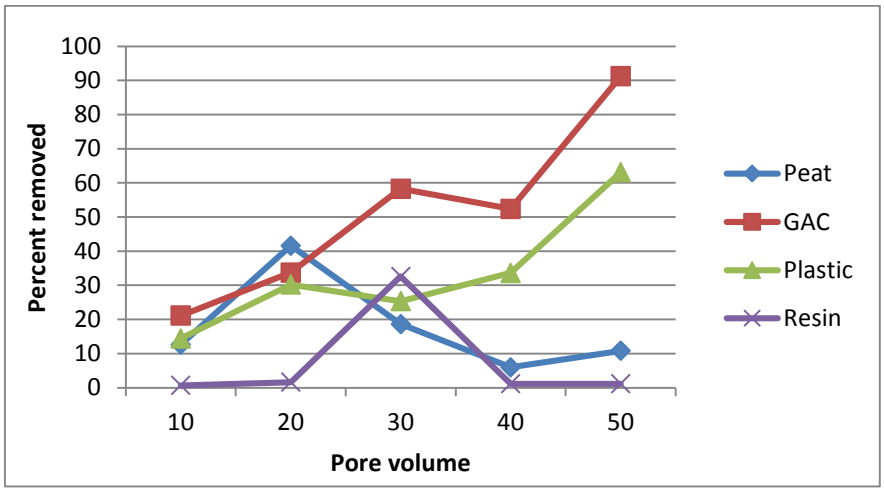

Figure 14. Percent removal of Cu as a function of treatment.

Lead removal was not effective for any of the sorbent treatments (Fig. 7). The maximum Pb removal was in GAC at 40 pv (37%). Peat was a poor sorbent for Pb. In a study by Shakeri and Valizadeh (2012) Pb was removed by peat by 92.5%. Sorption rate was affected by particle size of the sorbent (Charkravarty, 2010; Benhima, 2008).

The resin was most effective in removal of Pb from the fracking fluid, compared to that for all other contaminints (Fig. 15). The resin removed 12% (50 pv) to 22% (30 pv) Pb from the fracking fluid.

The poor removal by all sorbents may be due in part to the low pH of the fracking fluid (Table 1). It is easier for sorbents to remove metals with a higher pH compared to a lower pH (Vijayaraghavan and Rajasekhar, 2005).

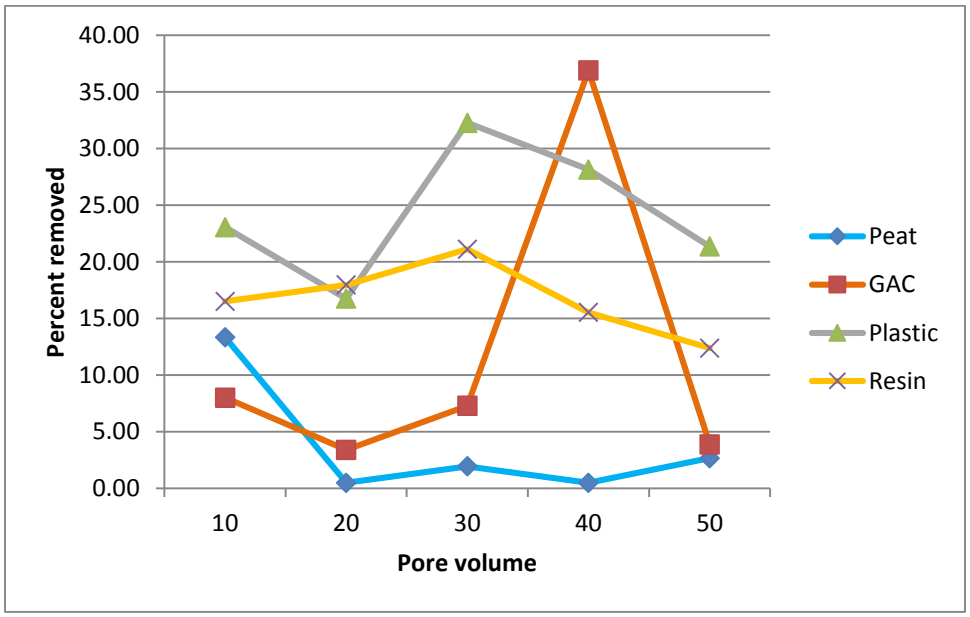

Figure 15. Percent removal of Cu as a function of treatment.

Greenhouse Study

Soil Properties

The Glynwood soil had a pH of 6.7 (Table 7). Total C and N contents were 3.9 and 0.36%, respectively. Levels of metals were low and values were consistent with those for non-contaminated soil. Soil texture is a silt loam.

Table 7. Selected chemical and physical properties of the Glynwood soil used in the CW.

Parameter	Value
pH	6.7
Total N (%)	0.36
TOC* %	3.9
Bray-1 P (mg/kg)	13.0
K (mg/kg)	86.9
Extractable metals (mg/kg)	
Cr	0.09
Cu	0.22
Fe	32.4
Ni	0.31
Pb	0.50
Zn	9.80
Texture, %	
Sand	28.0
Silt	51.0
Clay	21.0

*TOC= Total organic carbon

Effluent Properties after CW Treatment

The pH of the fracking fluid was 4.1 before passage through the wetland (Table 6); after CW treatment the pH rose to 7.0 (Table 8). In contrast, however, effluent pH of the control (no cattails) was 6.7. The Glynwood soil is formed upon dolomitic limestone deposits (NRCS, 2016) and presumably has a substantial acid buffering capacity.

Salinity (as measured by EC) decreased substantially after CW treatment (Table 8). Values of EC were 2.9 uS/cm for Stage 1 and 3.3 uS/cm for Stage 2. This compares with 18.6 uS/cm for the control. In a study of CW treatment of high-salinity wastewater Jesus et al. (2014)

measured salinity reductions of 52%. Despite some growth inhibition, *Typha latifolia* plants remained viable, with 94% survival rate. Cattail, sedge, kallar grass, salt meadow cordgrass, water grass and Asia crabgrass were found to be capable of treating saline wastewater (Janen, 2010). According to Pantip and Suwanchai, (2004) both *Typha* and Asia crabgrass had the ability to survive and absorb nitrogen and remove substantial BOD from saline wastewater.

Copper concentrations in the effluent after Stages 1 and 2 ranged from 0.03-0.04 mg/L (Table 8), which was a 76% reduction from the HFF concentration, 4.45 mg/l (Table 6). Total Pb concentration was 0.69 (Stage 1) and 0.76 (Stage 2). These values are a 68% decrease from the Pb concentration in the HFF (4.12 mg/l) As pH increases from 5.5 Pb decreases. The observed Pb concentrations are slightly lower than levels in the control (no cattails) (0.88 mg/L). In a study by Lesage et al. (2007) the percentage of Cu removal was 48.3%, and Pb removal was 81% . Khan and Shah (2009), using *Typha*, noted a Pb removal rate of 50%.

Table 8. Chemical properties of effluents from constructed wetland after 45 days.

	pH	EC	Na	K	Mg	Cu	Pb
		µS/cm	---------- mg/l ----------				
Stage 1	7.02	2.90	2.66±0.60	1.0±0.37	3.07±0.36	0.03±0.01	0.69±0.26
Stage 2	7.05	3.30	3.10±1.10	1.31±1.01	2.95±0.14	0.04±0.02	0.76±0.23
Control A	6.69	18.60	3.26±0.77	2.13±1.08	4.57±0.17	0.02±0.01	0.03±0.01
Control B	8.20	0.84	4.27±0.02	4.87±0.01	2.28+0.15	0.20+0.21	BDL*

Control A = Flushed with HFF; no cattails.
Control B = Flushed with H_2O; with cattails.
*BDL = below detectable limits.

Arroyo et al. (2010), studying the efficacy of an artificial wetland system treating wastewater, found a wide range of removal efficiencies, including 48% reduction in Pb. Walker and Hurl (2002), monitored wetlands treating storm water for Zn, Cu, Pb, Cr, and arsenic (As) over a four-month period. They found As, Pb and Cu were reduced by 57, 71 and 48% respectively. Walker and Hurl (2002) found some metal levels decreased while others increased. They found that the heavy metals were particularly associated with organic matter in the CW. Therefore, they concluded that adsorption and sedimentation were the primary processes for removal, although filtration by plants, adsorption, biological assimilation, decomposition, chemical transformation, and volatilization are also significant removal processes.

Biomass Production of *Typha latifolia*

Shoot production of *Typha* was substantially greater in the HFF-treated cells as compared with the control (Table 9). Total dry mass production was 18.3 and 18.9 g in Stages 1 and 2, respectively, compared with 1.7 g in the control. It is possible that, although toxic components occurred in the fracking fluid, the high concentrations of K and Mg were sufficient to compensate and even enhance plant growth. Woo and Zedler (2002) and Svengsouk and Mitsch (2000) studied the effect of nutrients on vegetative growth of *Typha spp*. They found that vegetative growth of *Typha* is increased by addition of nutrients, and that *Typha* can quickly form monotypic stands in fertile wetland systems.

In Stage 1 root biomass production was markedly low compared with that for Stage 2 and the control (Table 9). It is possible that, being the first plants to contact the fracking fluid, *Typha* roots were adversely affected by Pb. Many plants will form Pb-phosphate and other lead

complexes in roots to prevent uptake; however, root growth may suffer (Blaylock and Huang, 2000 , Munzuroglu and Geckil, 2002).

Southern cattail (*Typha domingensis*) is highly salt-tolerant (Khider et al., 2012; Mojiri et al., 2013).

Table 9. Total dry mass production of *Typha latifolia* in constructed wetland.

	Shoots	Roots
	------- g -------	
Stage 1	18.30	2.50
Stage 2	18.90	7.20
Control	10.70	6.60

Soil Chemical Properties after CW Treatment

Mean soil pH in Stage 1 was 6.67, and 7.06 for Stage 2 (Table 10). This compares with a pH of 4.18 in the control (no *Typha*). Soil pH is important when determining the extractable metal content in the soil. pH influences the absorption rate of metals -- the higher the pH, the higher the adsorption rate (Zhang and Zhou, 2011). Soil pH is very important when growing plants as well – the optimum pH value for most green plants is approximately neutral. At this pH level most nutrients are optimally available.

The control treatment had a substantially higher EC level than did Stages 1 or 2 (Table 5). These data demontrate the effectiveness of *Typha* in trapping or otherwise removing free salts from the soil solution.

Table 10. Chemical properties of soil in constructed wetlands after 45 days. (Mean+SD)

Treatment	pH	EC	Na	K	Cu	Pb
		µS/cm	---------- mg/l ----------			
Stage 1	6.97	2.9	0.19± 0.29	0.64± 0.01	1.02± 0.23	0.61± 0.38
Stage 2	7.06	3.3	0.28 ± 0.17	0.38 ± 0.05	0.20 ± 0.07	0.28± 0.17
Control	4.18	22.1	4.27± 0.02	4.87± 0.01	3.20 ± 0.21	4.24 ± 0.26

Control = Treated with HFF; no cattails

Soil Cu concentrations measured 1.0 and 0.2 mg kg^{-1} in Stages 1 and 2, respectively (Table 5). The Glynwood soil used in this experiment contained 3.9% TOC, which provides a moderate sorption capacity for metals.

Soil Pb concentrations measured 0.61 (Stage 1) and 0.3 mg kg^{-1} (Stage 2), compared with 4.24 mg kg^{-1} in the control (no cattails). This result is likely due to Pb uptake by *Typha*. It is also possible that Pb has precipitated out of solution in Stages 1 and 2. Metals introduced to wetlands are either in particulate or dissolved forms. Wetland sediments are generally considered a sink for metals (Arroyo et al., 2010; Burton and Scott, 1992) and may contain very high concentrations of metals in a reduced state (Weis and Weis, 2004). The major processes responsible for metal removal in wetlands include adsorption to sediments and soils, precipitation as insoluble salts, and uptake by plants and bacteria (Kadlec et al., 2010). Plant activities influence and modify the distribution of trace metals between the solid and aqueous phases (Bucher, 2012).

Metal Uptake and Accumulation by *Typha*

Sodium content of *Typha* shoots was 15.1 and 95.3 mg kg^{-1} in Stages 1 and 2, respectively (Table 11). This compares with 35.8 mg kg^{-1} in the control. Vymazal and Sveha (2012) found, using a constructed wetland, that Reed canarygrass (*Phalaris arundinacea*) accumulated 20,376 mg kg^{-1} Na, and common reed (*Phragmites australis*) accumulated 15,606 mg/kg. The authors stated, however, that neither species was effective in retention of the studied elements. Removal Na averaged only 7.4. Sodium belongs to the so-called "beneficial elements," as it is not generally required by plants (Hopkins, 1999). Brownell and Crossland (1972) reported that Na is generally essential as a micronutrient for C_4 plants and in lower concentrations for most C_3 plants. Most freshwater wetland macrophytes have low Na requirements, with concentrations in the aboveground biomass lower than 2,000 mg kg^{-1} (Boyd, 1978; Vymazal, 1995).

Typha shoots contained 3.7 and 2.9 mg kg^{-1}Cu, respectively in Stages 1 and 2 (Table 11). This compares with 0.9 mg kg^{-1} Cu in the control. Using a constructed wetland, reduction of Cu was 77% (Bandaruk, 2013). Knox et al., (2010), Vymazal, (2005a) and Kröpfelová et al., (2009) stated similar results in their studies. Copper was retained with a similar average retention of 52% by Arroyo et al. (2010), a result not in accordance with other studies such as those by Lesage (2006) or Gersberg et al. (1984) who reported higher copper removal in HF CWs (> 90%). Other systems presented retention of copper slightly higher, such as those by Scholz (2004) in different experimental vertical-flow constructed wetlands, or Scholes et al. (1998) in a surface flow system.

Copper uptake in the roots was slightly greater than that for shoots -- 5.8 and 3.6 mg kg^{-1} were measured in Stages 1 and 2, respectively (Table 12).

Shoots of *Typha* accumulated almost as much Pb as did roots (24.7 versus 36.8 mg kg^{-1}, respectively, in Stage 1) (Tables 11 and 12). Concentrations of Pb in the plant were higher than the average concentrations reported as phytotoxic (< 5 mg/kg) by Markert (1992). Kabata-Pendias and Pendias (2001) reported that Pb contents of plants varied between 0.05 and 3.0 mg/kg. Ye et al. (1997) found Pb in *Typha latifolia* leaves to range from 4.7-40 mg kg^{-1}; however, the amount in roots varied widely (25-3628 mg kg^{-1}). Carranza-Alvarez et al. (2008) reported Pb concentrations ranged from 10 to 25 mg kg^{-1}, and the maximum accumulation of Pb was detected in roots. Dunbabin and Bowmer (1992) reported metal concentrations in *Typha* to increase in the following order: roots > rhizomes > non-green leaf > green leaf.

Table 11. Metal uptake by *Typha* shoots in constructed wetlands after 45 days. (Mean±SD)

	Na	K	Cu	Pb
	---------- mg/kg ----------			
Stage 1	15.16± 3.70	25.64± 0.76	3.68±0.90	24.74±6.21
Stage 2	94.32±35.30	142.36±35.80	2.92±0.40	22.92±7.07
Control	35.78± 1.40	105.54±4.76	0.9±0.20	1.45±0.20

[a]Means followed by a different letter are statistically significant ($p < 0.05$).

Table 12. Metal uptake by *Typha* roots in constructed wetlands after 45 days. (Mean±SD)

	Na	K	Cu	Pb
	---------- mg/kg ----------			
Stage 1	114.48±55.4	48.24±0.04	5.84+1.10	36.82±2.27
Stage 2	51.62±16.80	91.16±0.26	3.64+0.80	16.7±0.10
Control	16.74±2.10	40.86±0.26	1.1±0.50	2.12±0.10

Typha tolerates enhanced levels of metals in its tissue without serious physiological damage (Sasmaz et al., 2008). Many plants possess specific mechanisms to enhance metal bioavailability and accumulate metals in roots (Romheld and Marschner 1986). Such mechanisms involve blocking the binding of ions to ion carriers. This association often results in decreased plant growth (Pahlsson 1989); however, *T. latifolia* grew well and tolerated high Pb concentrations.

Various grass species are considered as metal excluders, as they accumulate large quantities of metals in roots; examples include *Lolium perenne* and *Brachiaria decumbens* (Santos et al. 2007; Golda and Korzeniowska 2016). Previous reports have also indicated the root uptake potential of *V. zizanioides* (Chen et al. 2004; Danh et al. 2009). This monocot could control the release of heavy metals into the environment by taking up available forms via the roots and stabilize them in situ.

Transfer factors

The transfer factor (TF) can be used to estimate a plant's potential for phytoremediation purposes. In the present study, *Typha* had TF <1 for Pb the first stage of the CW (Table 13). TF values < 1 indicate low metal translocation to shoots. These data are consistent with results for terrestrial plants grown in other metal-contaminated soils (Meeinkuirt et al., 2012; Phaenark et al., 2009). Transfer factors of metals in *T. latifolia* ranged between 0.39 and 1.18 in a study by Sasmaz et al. (2008). Sasmaz et al. (2008) found that *T. latifolia* did not effectively transfer heavy metals (Co, Cd, Cr, Pb, Cu, Ni, Zn) from root to shoot. Different plant types have markedly different physiologies, which results in different translocation potential for metals (Chen et al., 2004). Kaewtubtim et al. (2016) found translocation values (TF) between roots and aboveground parts (leaves and stems) to range from 0.2 - 4.4 for Cu and 0.1 - 7.9 for Pb, respectively. Mojiri et al. (2013) measured a TF = 1.0 for using *Typha domingensis.* This plant was an effective accumulator plant for phytoremediation of several heavy metals.

Table 13. Transfer factors (TF) for Na, Cu and Pb in *Typha latifolia*.

	Na	Cu	Pb
Stage 1	0.13	0.63	0.67
Stage 2	1.83	0.80	1.37
Control	2.14	0.77	0.81

High metal concentrations in roots combined with TF values < 1 indicate the potential of the plant for well-balanced metal accumulation and translocation (Haque et al., 2008). In order for a plant growing on contaminated soil to avoid metal toxicity, sequestering the metal in the root serves as an appropriate metal exclusion strategy (Marques et al., 2009). There is evidence of plant mechanisms which allow roots to accumulate high levels of trace metals as compared with other plant parts (MacFarlane et al., 2003; Naidoo et al., 2014). This phenomenon was detected in mangrove species such as *Avicennia marina, Rhizophora* spp., and *Kandelia* spp. (Peters et al., 1997) and is consistent with data for the present study.

The extent of metal accumulation depends upon both plant mechanisms and sediment chemistry (Chaudhuri et al., 2014). Aerial roots of many plant species diffuse oxygen into the substrate such that oxidation occurs in the rhizosphere, resulting in metal accumulation in fine roots (Chaudhuri et al., 2014; Machado et al., 2005; Marchand et al., 2011). The large surface area and high density of the root system may encourage metal uptake, along with adsorption of metals subsequent to oxidation of metal sulfides (Lacerda et al., 1992, 1993; Marchand et al., 2011; Otero et al., 2006).

In the present study, *Typha* had TF = 1.4 for Pb in the second stage of the CW. Kaewtubtim et al. (2016) found highest TF values in stems of *D. trifoliata* (7.9 for Pb). Plants with TF values > 1 have a high efficiency of translocation of metals from roots to aboveground parts (Murray et al., 2009). This effect is most likely due to efficient metal transporter systems (Zhao et al., 2002), and probably sequestration of metals in leaf vacuoles and apoplast (Lasat et al., 2000). Baker (1981) and Zu et al. (2005) reported that TLFs higher than 1.0 were determined in metal accumulator species whereas TL factors were typically lower than 1.0 in metal excluder species. TF values higher than 1.0 indicates an efficient ability to transport metal from root to

leaf, most likely due to efficient metal transporter systems (Zhao et al., 2002), and probably sequestration of metals in leaf vacuoles and apoplast (Lasat et al., 2000; Sasmaz et al., 2008).

Bioconcentration Factor (BCF)

Typha shoots had BCF values for Pb ranging from 2.9 (first stage) to 8.0 (second stage) (Table 14). *Typha* roots had BCF >1 in both CW stages for Pb (4.19 in the first stage and 5.82 in the second stage), indicating its potential for high capacity for Pb absorption from sediments to plant tissue (Table 15).

Table 14. Bioconcentration Factors (BCF) for Na, Cu and Pb in *Typha latifolia* shoots.

	Na	Cu	Pb
Stage 1	5.4	0.71	2.8
Stage 2	2.2	2.8	8.0

Table 15. Bioconcentration Factors (BCF) for Na, Cu and Pb in *Typha latifolia* roots.

	Na	Cu	Pb
Stage 1	40.9	1.1	4.19
Stage 2	1.2	3.5	5.82

BCF values for shoots > 1.0 indicates an ability of the plant to absorb and transport metals from sediment and then stored them in their above-ground part (Baker et al., 1994; Brown et al., 1994; Wei et al., 2002). Kaewtubtim et al. (2016) found BCF values of Vetiver leaves ranged from 0.4-9.0 for Cu and 0.2-22.7 for Pb. In this study, *Typha latifolia* may be categorized as a Pb accumulator as it has TF and BCF values > 1 (except for Stage 1, where TF = 0.67).

Typha plants in the first stage of the CW experienced lower TF and BCF values (Tables 13 and 14). Ye et al. (1997) found that *Typha* plants grown in metal-contaminated media accumulated considerably more metal (up to nearly twice as Pb) in roots than the uncontaminated population. Their data do not support the hypothesis that populations from metal-contaminated sites have evolved tolerance to Pb and other metals, but rather that *T. latifolia* shows constitutional tolerance.

Table 16. Uptake of Na, Cu and Pb by *Typha latifolia* shoots.

	Na	Cu	Pb
	---------- mg ----------		
Stage 1	277.00	67.20	452.00
Stage 2	1784.50	55.20	433.60
Control	382.10	9.60	155.70

Table 17. Uptake of Na, Cu and Pb by *Typha latifolia* roots.

	Na	Cu	Pb
	---------- mg ----------		
Stage 1	280.50	14.30	90.20
Stage 2	370.10	26.10	119.70
Control	111.00	7.30	14.10

The ability of *Typha* shoots to take up soil Pb is considerable (Table 10) – Pb concentration in shoots is more than four times that in the roots. The same is true for Cu removal, at least in the first stage. The quantity of Na absorbed by *Typha* roots is substantial – 1784 mg Na was removed in Stage 2. These data demonstrates the capability of *Typha* for possible phytotreatment of hydraulic fracturing fluids.

CONCLUSIONS

Heavy metal enriched wastewater has been a great concern to oil and gas producing companies. Most oil companies spend substantial funds purchasing water, and also recycling wastewater. Recycling of wastewater is a continuous, long-term process which requires an efficient system.

In the present study, GAC and peat were moderately successful in increasing pH of the hydraulic fracturing fluid and in removing Na. Results were of limited value for Cu and Pb

removal. Sorbent treatment of hydraulic fracturing fluid was of little overall success, regardless of the type of sorbent. One of the key issues for sorbent treatment appears to be concentration of the contaminant(s) of interest -- sorption treatment is not effective for removal of very high concentrations of Na, K, Pb, etc. The sorption technique is commonly employed as a polishing step during wastewater treatment, rather as the initial treatment process.

In the constructed wetland, pH of fracking fluid increased from 4.1 to 7.0 and electrical conductivity decreased significantly. The plants grown in both stages produced substantial biomass, perhaps from a potent dose of K and Mg. Transfer and bioconcentration factors indicate that *Typha* may be effective for metals removal from hydraulic fracturing fluids. The reported study may be of significant practical value to oil and gas production industries which generate large quantities of contaminated oil and gas wastewater.

SUGGESTIONS FOR FUTURE RESEARCH

Based on the completed study, a number of questions and new research directions have arisen.

Constructed wetland substrates will change over time. For example, organic matter will accumulate, and the substrate may become more anaerobic. In addition, toxins such as Na and Pb will accumulate. These changes will likely affect the efficiency of metals and salinity removal. It is therefore proposed that future studies take place over a significantly longer period, e.g., two to three years in order to assess the long-term field potential for treatment of fracking fluids.

Constructed wetlands could be established using different growth media for the plants. For example, in addition to using soil, other treatments could include peat and various types of

compost. The published literature reveals a range of treatment efficiencies for metals removal in these various media. Some media have higher exchange capacities; others may promote anoxic conditions and therefore enhance metal precipitation.

Different wetland plants could be employed in CWs. For example, various species of sedges are potentially able to tolerate the salinity posed by hydraulic fracturing fluids. It is possible that sedges may also accumulate metals. Likewise, different species of *Typha*, in addition to *Typha latifolia*, should be assessed for their ability to uptake metals.

The slow escape of liquids from CWs via infiltration over the long-term is a concern as there is the potential for risks to groundwater quality. Therefore, soil and groundwater monitoring should be conducted as part of a CW study.

CW design should be taken into consideration. Different designs for wetlands should be looked into to determine which is ideal for each different setting and wastewater type.

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APPENDICES

Table A.1. Chemical composition of HFF leachate after treatment in peat.

PV	pH	EC	Pb	Cu	Na	K	Mg
			mg/l				
10	6.03±0.02	17.02±0.04	0.55±0.03	1.54±0.23	1.54±0.23	3.47±0.31	0.55±0.55
20	6.94±0.60	17.51±0.14	0.02±0.01	1.92±1.72	1.92±1.72	3.24±0.12	1.81±1.71
30	6.14±0.11	24.23±2.25	0.08±0.07	1.81±1.80	1.81±1.80	3.39±0.23	0.81±0.70
40	6.17±0.09	17.00±3.32	0.02±0.01	1.55±0.71	1.55±0.71	3.57±0.39	0.26±0.04
50	6.32± 0.19	19.08+1.92	0.11±0.09	1.74±0.32	1.74±0.32	3.56±0.25	0.47±0.21

(Mean±SD)

Table A.2. Chemical composition of HFF leachate after treatment in activated charcoal.

PV	pH	EC	Pb	Cu	Na	K	Mg
			mg/l				
10	7.04±0.04	13.38±2.00	0.33±0.55	0.09±0.05	3.72±0.21	4.03±0.43	4.03±0.43
20	7.27±0.17	16.26±0.83	0.14±0.06	0.19±0.08	3.52±0.30	4.92±0.01	4.03±0.43
30	7.37± 0.18	15.45±0.69	0.30±0.08	0.16±0.04	3.42±0.28	4.73±0.44	4.03±0.43
40	7.15± 0.12	12.15±1.04	1.52±0.89	2.22±0.85	3.22±0.66	4.56±0.17	4.03±0.43
50	7.40±0.29	14.73±0.62	0.16±0.17	1.84±1.10	3.02±0.52	3.89±0.65	4.03±0.43

(Mean±SD)

Table A.3. Chemical composition of HFF leachate after treatment in shredded plastic

Sampling	pH	EC	Pb	Cu	Na	K	Mg
	---------- mg/l ----------						
10	6.02±0.02	17.65±0.10	0.95±0.67	1.62±1.03	3.19±0.91	3.19±0.91	0.03±0.02
20	6.34±0.39	17.48±0.20	0.69±0.39	1.51±0.94	0.33±0.55	2.95±0.70	0.07±0.04
30	6.17±0.11	17.57±0.56	1.33±1.28	3.35±0.16	0.33±0.55	3.33±0.17	0.20±0.34
40	6.55±0.14	18.10±0.71	1.16±0.05	2.23±0.45	0.33±0.55	0.34±0.16	0.05±0.04
50	6.67±0.17	19.60±1.52	0.88±0.65	1.01±0.01	0.33±0.55	3.36±0.07	0.05±0.03

(Mean±SD)

Table A.4. Chemical composition of HFF leachate after treatment in synthetic resin.

PV	pH	EC	Pb	Cu	Na	K	Mg
	---------- mg/l ----------						
10	6.23±0.12	15.69±1.0	0.68±0.36	0.11±0.01	0.09±0.17	0.09±0.08	0.10±0.02
20	6.23±0.66	15.31±0.42	0.74±0.61	0.07±0.05	0.07±0.03	0.07±0.05	0.57±0.04
30	6.79±0.41	15.70±0.37	0.87±0.91	0.05±0.05	0.05±0.05	0.07±0.08	0.20±0.34
40	6.87+0.13	16.80±0.70	0.64±0.60	0.10±0.07	0.18±0.20	0.02±0.01	0.60±0.04
50	7.02±0.21	17.18±0.20	0.51±0.51	0.04±0.04	0.87±1.07	0.86±0.41	0.63±0.03

(Mean±SD)

LIST OF SYMBOLS

BCF……..…Bioconcentration factor

Cr…….……Chromium

Cu……...……...Copper

CW…….....Constructed wetland

EC……Electrical conductivity

GAC…….Granular activated carbon

HFF……...……Hydraulic fracking fluid

IUPAC…….... International Union of Pure and Applied Chemistry

K……..…….Potassium

Mg……..……Magnesium

Na…….……Sodium

Pb……...…….....Lead

pv…….……....Pore volume